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Metallurgical Project

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ENGINEERING DEVELOPMENT SECTION

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FINAL REPORT

PROBLEM ASSIGNMENT NO. 223-X18E

DISPOSAL OF ACTIVE WASTE SOLUTIONS

15 July 1944

* * *

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D. McGhee
For: M. T. Bray, Supervisor Laboratory Records Dept. ORNL

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ABSTRACT

The Engineering Development Section has, by request, submitted a recommendation for the design and operation of a new settling basin for removal of active sludges from plant wastes. Experimental work has been carried out to determine the probable performance of such a basin. Important results are:

1. If a 35:1 dilution of the waste from W-6 (by-product waste) with plant cooling water is made, one day's quiet settling should give a 10-fold decontamination, and one week's settling possibly 20-fold.

2. A 30-fold decontamination can be attained by percolation through local soil, but percolation rates are very low.

3. A 35:1 dilution ratio is better than 100:1 or 150:1.

4. The basin actually installed departed somewhat from the recommendation and gives (as of July 14) a 4-fold decontamination, or a maximum discharge from the plant of about 1-1/2 curies/day. The safe limit has been set at 1 curie/day on a basis so conservative that 1-1/2 curies/day is not considered excessive. Therefore, no changes in the installation or its operation are at present contemplated by the Plant Division.

5. The useful life of the installation will be limited by the rate of accumulation of sludge in the basin. A life of 6 months or more seems likely under present conditions.

INTRODUCTION

Original plans for the operation of the separation area called for complete retention of the by-product waste solutions as well as the metal waste. Tanks were provided for a few years hold-up based on the lanthanum fluoride decontamination process. However, by-product separation was started with bismuth phosphate precipitation giving much larger volumes of waste solutions.

No commensurate expansion of storage facilities was undertaken since by that time it was considered feasible to dilute the waste solution with water used for cooling cell vessels and dispose of the mixture off the plant.(1) The tanks already built would have enough capacity to allow 20-fold decay of the activity so that the plant flow could be diluted to below the tolerance level of $\sim 10^{-11}$ watts/cc (0.1 r/24 hours for a completely immersed body) using water at the rate of 250 gpm. The cooling water flow was between 200 and 500 gpm so that adequate dilution was available. This water was being used for diluting mild activity from floor washings and final decontamination steps and was monitored in the east and west ponds (Fig. 1) before discharging to the White Oak Creek drainage system.

Disposal of the oldest by-product waste by dilution was begun March 6(2) and continued until April 27, 1944 (Flowsheet dotted lines, Figure 1). During this period, it was observed that dilution caused the formation of a gelatinous precipitate which settled out to a certain extent in the ponds. Analyses showed that a large part of the activity was in the precipitate and that the mud in White Oak Creek and Reservoir was accumulating activity. When accumulation was stopped, it had not reached a dangerous level, but possibly would have done so if allowed to continue.

An immediate solution to the problem of handling the activity was required since the last of the four by-product waste tanks (W5, W6, W7, W8 (Fig. 1)) would be full early in July and since one of these would have to be emptied again by the middle of September in order to receive metal waste.

It was apparent that some decontamination system would have to be used since additional tanks for concentrated waste could not be built in time. The precipitate formed on dilution could be retained or chemicals added to the storage tanks for carrying down activity in a precipitate. For 10 days during April, $CaCl_2$ was added to W5 at the rate of 500 lbs. per day (.04% of total weight in tank per day); the effluent from this tank had been reduced to 40% of its former activity and the effluent from W6 to 70% of its original value(2).

It should be emphasized that the average activity of the waste discharged during this period was within the accepted activity tolerance; only the unanticipated precipitation (and hence concentration) of the activity in the creek bed caused concern. It was evident that some means of retaining this precipitate within the plant area would be a good answer to the problem, and a sedimentation system through which the diluted waste would pass was hurriedly designed. The following data were available at this time.:

(1) the precipitate formed is 3% by volume water used for dilution using 70-fold dilution and 24 hour settling time.
(2) the quantity of precipitate formed is proportional to the quantity of cooling water used as diluent. (No upper limit given.)
(3) the activity in the supernate from settling tests vs. dilution is

Dilution (fold)	70	35	14	7
Activity (% of initial)	12	12.5	15.9	29.2

(4) the waste discharged is about 5000 gallons per day.
(5) the rate of plant cooling water discharge is about 500,000 gpd.

Since little improvement in decontamination could be expected by increasing the dilution about 35-fold and since more space for precipitate would have to be provided if dilution were increased, it was decided that dilution should be set at 35-fold.

On May 5, accordingly, Mr. Feyder of the Project Engineers' Office was given the following proposal for his guidance in carrying out the Project requested in this connection by the Plant Division:

(1) Construction of a 1,000,000 gallon settling pond to be used in series alternately with the present 200,000 gallon ponds.
(2) Construction of a 300,000 gallon sludge storage basin with cover for receiving sludge from a 200,000 gallon pond not in series at the time with the proposed settling pond.
(3) A by-pass on the cooling water line to control the amount of dilution.

Figure 5 shows the proposal in more detail.

The scheme finally adopted differs from this proposal in that the capacities of the two basins were combined to give one deep basin into which the diluted waste flows directly from the point of mixing. Operation using uncontrolled dilution was begun July 2 jetting about 4000 gallons per day from W6. Beginning on the 5th, the flow was increased to 10,000 gallons a day. The complete operation is shown by the flowsheet, solid lines, Figure 1.

The new basin has been monitored at the diversion box and at each of the 5 discharge pipes every 4 hours since July 6. Figure 2 is a record of the activities at the diversion box and of the average of the values at the discharge pipe up to July 14. Little variation in flow is found from pipe to pipe. The diversion box values average about 330 counts per cc per minute as they should for a W6 flow rate of 10,000 gallons per day diluted with 900,000 gallons of cooling water per day. Estimates place the diluent flow rate between 500,000 and 900,000 gallons per day (350 and 600 gpm).

Discharge activity may still be increasing. For the 13th and 14th, it was in the region of 80 counts per cc per minute showing a basin performance of 4-fold. Using this factor, a maximum of about 1-1/2 curies per day are being discharged to White Oak Creek or a little higher than the 1 curie considered probably safe by J. G. Hamilton[(3)]. (See Appendix A).

Tests for an immediate solution of the problem of decontaminating the waste are considered complete. R. S. Apple and M. D. Peterson report that over-all factors of twenty very probably can be obtained by addition of 1% or less of $CaCl_2$[(4)]. The Engineering Development Section has found that with proper dilution at least 10-fold decontamination can be realized even without $CaCl_2$ addition. These factors would result in less than 1 curie a day in the effluent from the plant.

The desirability of a program to devise a more permanent means of waste disposal for Clinton is not clear, in view of the uncertainties surrounding plant operation here six months hence. However, if such a program is desirable, it should be started now.

In connection with estimating the probable performance of the new basin, the Engineering Development Section has performed a series of tests to find (1) the average properties of the precipitates formed from cooling water obtained over a period of time, (2) the effect of various clays as coagulants, (3) the change in the colloidal nature of the precipitate with degree of dilution, (4) the ability of local soil to hold activity if seepage from the basin occurs. These tests are reported below.

SETTLING RATE TESTS

Standard Tests

Tests were performed once or twice a week from May 5 to July 2 in order to average variations in decontamination and amount of precipitate resulting from changes in cooling water. The tests also served the purpose of discovering the effects of unusual water conditions such as turbidity. The amount of cooling water added was fixed at 35 times the amount of solution since, as indicated previously, little improvement in removal of activity occurs at greater dilution.

The tests were performed as follows: Cooling water from the influent to East Pond was mixed with solution from the surface of W6 liquid in the ratio of 35 to 1 and immediately poured into six 50 to 60 mm glass columns, 4 feet high. One composite sample above the one foot level was taken from each of the columns at times 1, 2, 4, 8, 24, and 168 hours after filling. An aliquot (50 cc) of the 500 cc sample was submitted to the Analytical Division for a total beta count.

The rate of "settling" of the activity is plotted on Figure 3 (Appendix). Although the results of the tests differ widely when compared at times up to several hours, they group closely later to indicate an average of 10-fold decontamination after 1 day settling time. The points for tests begun on May 12 and 17 fall near 2 parallel straight lines suggesting about 20-fold decontamination after 1 week's retention time. The run begun May 15 with turbid cooling water obtained after a heavy rain shows better decontamination than the other runs only for short settling times (curved line, Figure 3).

All of the precipitates had about the same gelatinous character, not unlike $Al(OH)_3$. Immediately upon dilution, the liquid became slightly milky. After about 30 seconds, flocculation was discernible and the precipitate began to settle although the milky, or hazy, appearance persisted for 30 to 60 minutes. Settling was unhindered, the flocs gradually thinning out over a period of roughly 2 hours. In all the tests, some of the particles stuck to the walls of the columns but were loosened when the liquid level in the column was lowered.

An unusual situation developed during the test begun on May 31. The flocs were seen to have occluded small air bubbles about the size of those formed while filling the columns. After about an hour, the bulk of the precipitate had settled forming about 6% of the volume in the column; some flocs, however, were floating on the surface. They were still floating at the 8 hour sampling time, but the settled portion had compressed to less than 3 percent of the total volume.

The average amount of precipitate formed was 2% of the total volume. Except for the very light precipitates obtained around June 1, the volume decreased very little after the bulk of the flocs had settled.

Tests with Additives

Three tests were made with possible coagulants in the hopes of improving settling rate and/or decontamination. The procedure was as folllows: tap water in 105E Building was mixed with clay or mud before the W6 solution was added; one run was made with bentonite added, another with kaolinite and a third with mud used in seepage tests. Six columns were filled and sampled as in the standard tests. The results shown by symbols B, K, and M on Figure 3 are typical of other runs at 35 to 1 dilution. These rather exploratory experiments showed no outstanding improvement in decontamination due to the use of these additives. The use of mud was suggested because nearly 30-fold overall decontamination was realized in seepage tests. Obviously more mud and longer contact time than was obtained in the column must be secured for this good decontamination.

Dilution Tests

One set of tests at various dilutions was performed to show how the colloidal properties of the precipitate changed and to confirm that the amount of precipitate increases with dilution. Tap water in 105E Building was used for 35, 100, and 150 to 1 dilution. Two columns were filled with each mixture for sampling at 24 and 80 hours.

Decontamination did not vary significantly between the two sampling times. For the 35 to 1 dilution the factor was 10 to 11-fold and for the greater dilutions, it varied between 5 to 7-fold. These latter dilutions showed about 2/3 the volume of precipitate per column as for the 35 to 1 which on a basis of a fixed amount of undiluted liquid means 2 to 3 times as much unpacked sludge.

Observation after filling the columns definitely established that the greater dilutions give more colloidal mixture, especially at 150 to 1 ratio. For this dilution, the milky appearance persisted for about 5 hours, fine flocs were much in evidence the next day and the precipitate on the walls did not loosen as the liquid level was lowered as always happened with the precipitates at the 35 to 1 dilution.

OTHER TESTS

Compaction of Precipitate

The effect of height on the volume of precipitate was tested to indicate what retention time may be expected in the new basin after several months operation. Several layers were allowed to accumulate in 3 columns, one containing precipitates typical of the standard tests, another also containing the clay and mud additives, and a final column using tap water as diluent for the precipitations. The percent decrease in height is plotted as a function of the unpacked height on Figure 4. The layers containing clays and mud account for the higher percent for the point farthermost from the line. This relationship probably holds down to 15 or 20%. The asymptotic value would be 5% assuming an unpacked density of 5 lbs per cu ft and a completely packed density of 100 lbs per cu ft.

Seepage Tests

Seepage tests were made to find the activity of any solution escaping through the earthen walls of the basin. Some mud was dipped from the southeast water table boring at the site of the new basin. For the first test, a bed 0.4 cm thick was formed on a No. 1 filter paper in an 8" Bückner funnel. Filtrate from a slurry formed by 35 to 1 dilution was added and suction applied. Seepage was collected in 150 to 500 cc portions and a 50 cc aliquot of each analyzed for total beta counts. A second test was run in like manner with a 1.5 cm bed of the same mud.

An average overall decontamination of 30-fold was found for a volume throughput 10 times the bed volume. Cracking of the bed prevented finding the volume throughput for saturation. There was little evidence of increased leakage at the end of the tests.

Seepage was imperceptible unless suction was applied. The flow rate obtained by nearly 700 mm of differential pressure was still very low, corresponding to 0.03 cm per day for a gradient of 1 cm of water per cm of soil.

PERFORMANCE OF NEW BASIN

Present Operation

As stated in the Introduction, present operation of the new basin is giving roughly 4-fold decontamination. Dilution is 90-fold or more and retention time in the basin is of the order of 1-2/3 to 2 days. When the tanks have been emptied, the dilution will increase at fixed cooling water flow to give a more colloidal precipitate, but the same retention time; it is expected that there will then be poorer decontamination.

As precipitate accumulates the retention time will decrease and again the decontamination may be affected adversely. After six months, it is probable that between 1 and 1.5 ft of precipitate will have formed cutting the retention time to somewhat over 1 day for a flow of 900,000 gal/day. The present basin discharge of 1-1/2 curies maximum may be expected to rise to around 2 curies when all the $CaCl_2$ treated solution has been emptied from W5 and W6 so that decontamination will become more important.

Controlled Dilution

Controlled dilution at 35 to 1 would be expected to give 10-fold decontamination during the period when 10,000 gallons are being diluted each day and possibly 20-fold when the necessary rate of disposal has dropped to around 5,000 gallons per day. The retention times would be 3 to 4 days at first, and 6 to 7 at the lower flow. The sludge formed will occupy about the same volume as for the greater dilutions because of the variation in packing of precipitate under its own weight.

Conclusions

Because of very low seepage rates, no trouble should be anticipated from leakage of activity through sides of the basin.

$CaCl_2$ treatment and/or dilution control should be provided to give a larger margin of safety in disposing of active, non-metal waste.

APPENDIX A

Waste Compositions, Activities, and Permissible Discharge

Waste Compositions: The non-metal chemical wastes are made up of "the waste solution from the aluminum coating removal, the solution of the two bismuth phosphate by-product precipitates, the waste supernatants from both the bismuth phosphate and the lanthanum fluoride product precipitates in the cells and the various wastes from the product concentration steps in Room D." (2) Chemical analysis of the precipitate formed on dilution is as follows:

> Calcium as CaO - 3.8%; iron as Fe_2O_3 - 2.0%; aluminum as Al_2O_3 - 12.5%; silicon as SiO_2 - 67%; magnesium as MgO - 2.1%; PO_4^{---} - 0.4%; and F^- - 26% (Reference 2).

Activities: These wastes contain about 10% of the fission activity, equal to 108 curies, based on a batch of one-third of a ton of metal containing 1 gram of product made in 100 days and cooled 40 days. With 20-fold cooling in the storage tanks and 1.2 days per batch, the activity to the new basin would be 4.5 curies per day in 4,700 gallons. Actually, around 5.7 curies in 10,000 gallons are being discharged per day based on 30,000 counts per cc per minute for W6 solution. This 5.7 value is about 60% of what it would be if the activity had decayed 20-fold in the tanks. The additional decontamination can be accounted for by the $CaCl_2$ treatment in W5 and W6 during April.

The specific activities in the W6 solution have been analyzed using a sample drawn from the surface of the tank on May 15(5). Another sample of W6 waste was diluted with 35 parts of plant water and the resulting precipitate and supernatant analyzed(4). The results are reproduced below.

Distribution of Activity

Element	W6 Solution		Precipitate		Supernate	
	Beta	Gamma	Beta	Gamma	Beta	Gamma
Cb	5%	39%	7 %	48%	12%	88%
Ce	21	0	46	0	7	0
Cs	3	0	0.3	0	16	0
Ru	8	3	0.6	0	58	10
Sr	1	-	2.3	-	0.9	0
Te	5	-	3.2	1.1	2	0.5
Zr	55	49	43	51	0.8	2
Y	2	-	-	-	-	-
La	.5	1	-	-	-	-
Ba	.2	-	-	-	-	-
Rare Earths	-	1	-	-	-	-
Total:	101%	93%	102%	100%	97%	101%

For the W6 sample, the beta counts were taken at 30 mg/cm^2 absorber and for the other samples at 50 mg/cm^2.

Permissible Discharge: These analyses together with others done at Berkeley form the basis on which Dr. J. G. Hamilton has made his recommendations for the permissible discharge of activities from the plant and from the White Oak Creek drainage system. Excerpts from a letter to Dr. Cantril(3) are as follows:

> "In view of the fact that both analyses of W6 wastes done at the site and here at Berkeley show small amounts of Sr, Te, Cs, and Ba together with the observation here that none of these four elements are present in significantly large quantities in the mud, it is my opinion that the tolerance problem is considerably simplified. Moreover, preliminary data in hand indicate that a very large proportion of the activity from these four elements is presumably fixed on the clay which should significantly reduce their absorption from the digestive tract."
>
> "Taking all of these facts into consideration, it would appear to me that the maximum daily amount of activity that can be released into the creek can be increased with safety to at least 250 millicuries a day and probably to one curie per day. Taking the higher figure and assuming a release of this quantity per day over a period of twelve months a saturation value for Zr and Cb of approximately 150 curies would be reached at which time, of course, the rate of loss of material by decay would be balanced by the rate at which fresh activity is introduced into the creek.
>
> "I would feel that this higher level of 1 curie per day would prove to be perfectly safe under the following conditions: first, that the drainage ditches and White Oak Creek be adequately fenced off and secondly, that less than an average of 100 millicuries a day be discharged from the mouth of the creek into the Clinch River. I feel this latter estimate is extremely conservative in view of the fact that the average rate of flow in the Clinch River is 200 cu ft per second. This factor of dilution would give a concentration of active material of the order of 2×10^{-10} curies per liter* when active material was being introduced into the Clinch River at the rate of 100 mc per day.

*Tolerance is about $\sim 10^{-6}$ curies per liter.

"It should be kept in mind that under the worst possible conditions, on the basis of a curie per day output into the White Oak Creek, the maximum amount of all radioactive material between the ponds and the Clinch River would be of the order of 200 curies. It seems to me extremely unlikely that a heavy flood would be able to wash all of this activity down into the Clinch River. However, should a flood of such magnitude occur, the rate of flow of the Clinch River would be so many times greater than the average 200 cu ft per second, that the active mud washed into it would be adequately diluted."

APPENDIX B

References and Other Reports on Waste Disposal

References:

(1) "Waste Disposal Report and Flowsheet", M. F. Acken, 1/19/44 (12/4/43).
(2) "Handling of Wastes from 205 Building (Up to May 1, 1944)," W. Q. Smith, 5/1/44.
(3) "Analytical Data from Berkeley," J. G. Hamilton to S. T. Cantril, 6/20/44.
(4) "Decontamination of Plant Neutralized Non-Metal Waste," R. S. Apple to W. C. Kay, 7/1/44.
(5) "Fission Product Analytical Report," R. I. Martens to M. C. Leverett, 5/27/44.

Other Reports:

(a) "Distribution of Radioactive Fission in Separation Plant Wastes," W. Q. Smith to J. G. Hamilton, 5/3/44.
(b) "Problem Assignment 223-X18E: Disposal of Active Waste Solutions," M. C. Leverett, 5/8/44.
(c) "Authorized Project C-36, 'Construct Settling Basin for Waste Water-Bldg. 206' ", M. S. Smith, 5/15/44.
(d) "Meeting on Decontamination of Chemical Wastes," W. Q. Smith to W. C. Kay, 5/20/44.
(e) "Analysis of Supernatant from W6," S. T. Cantril to J. G. Hamilton, 6/6/44.
(f) "Activity of Mud in White Oak Creek Drainage System," S. T. Cantril to F. B. Vaughan and B. C. Nylen, 6/20/44.

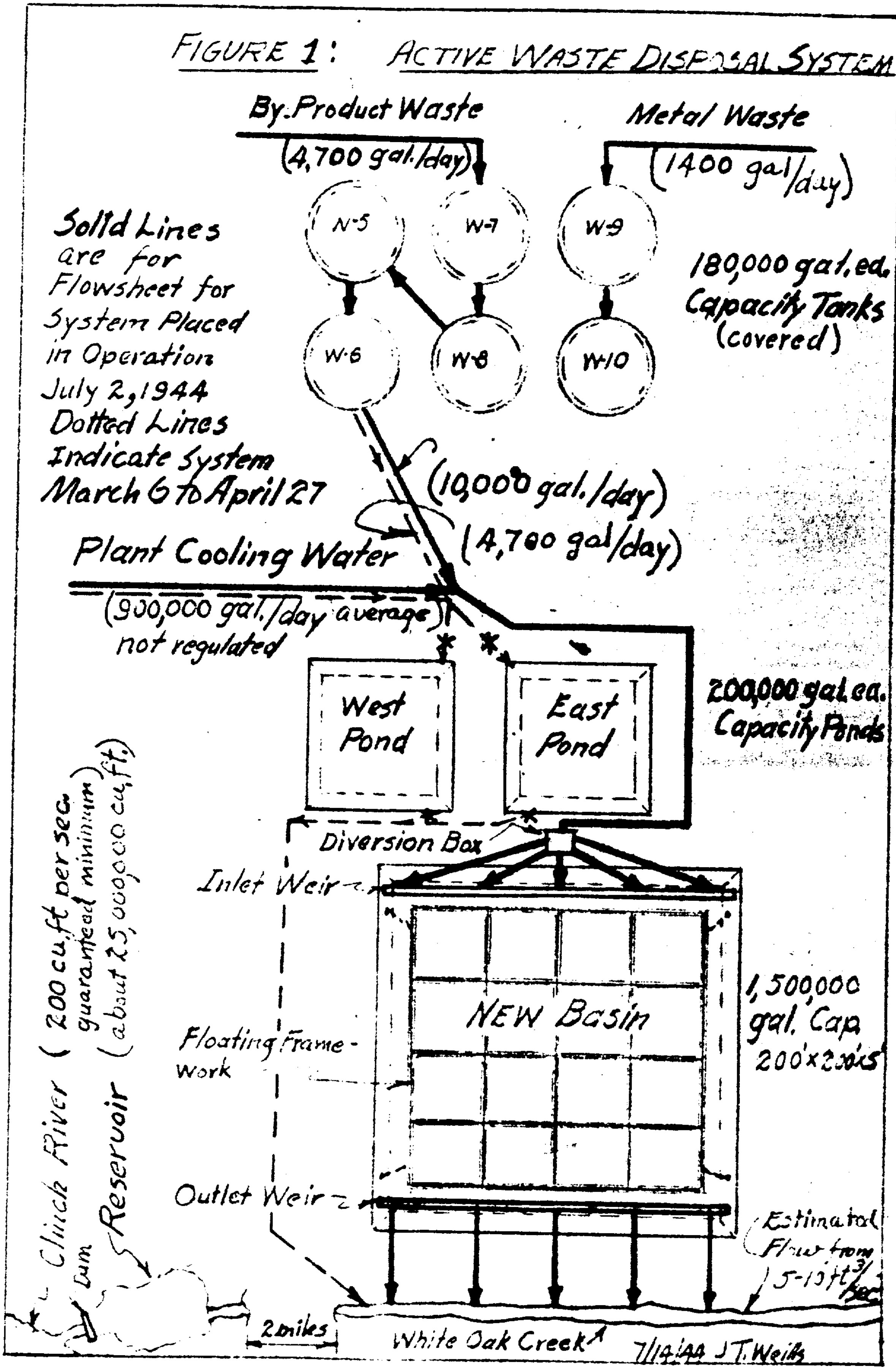
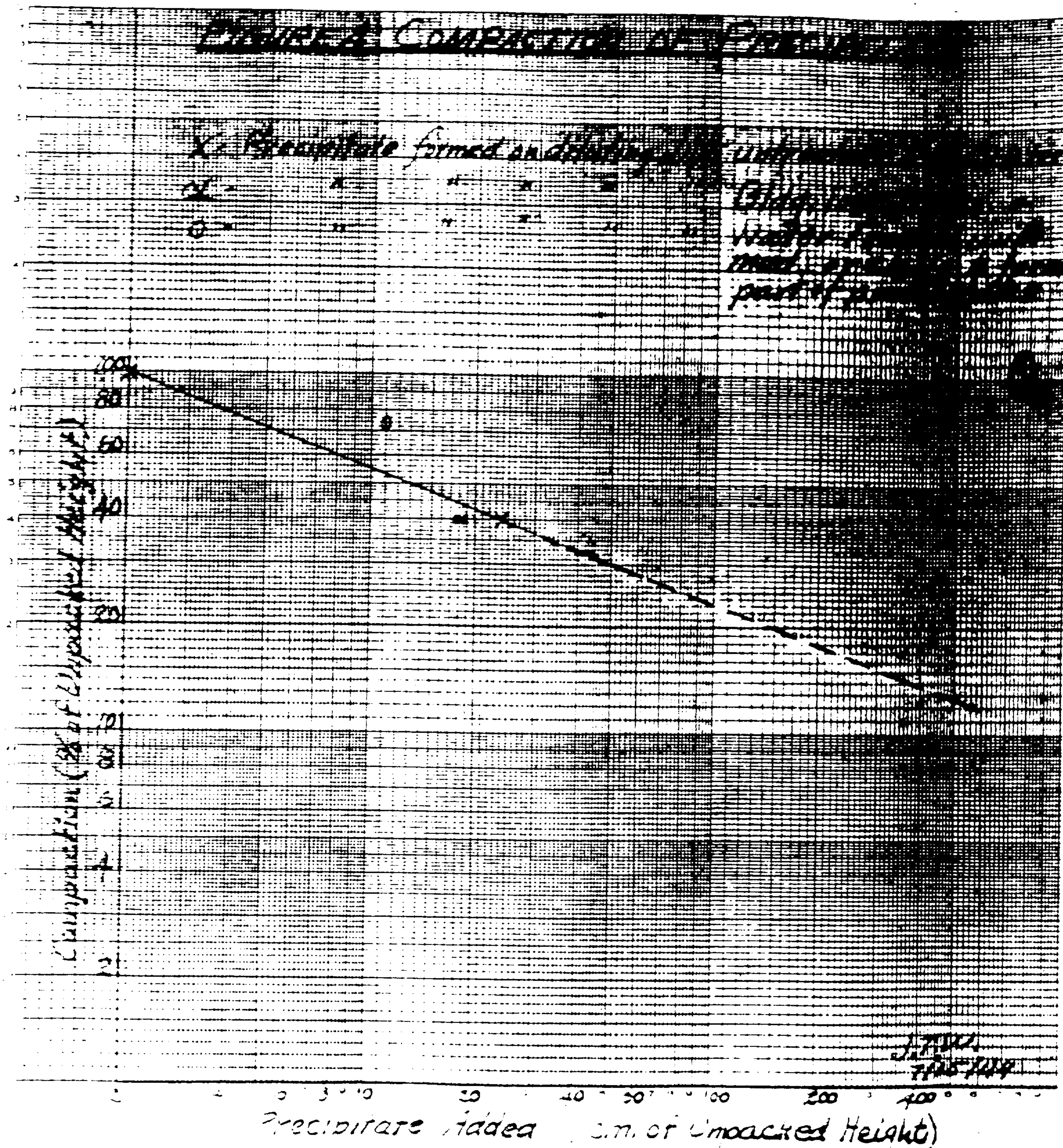
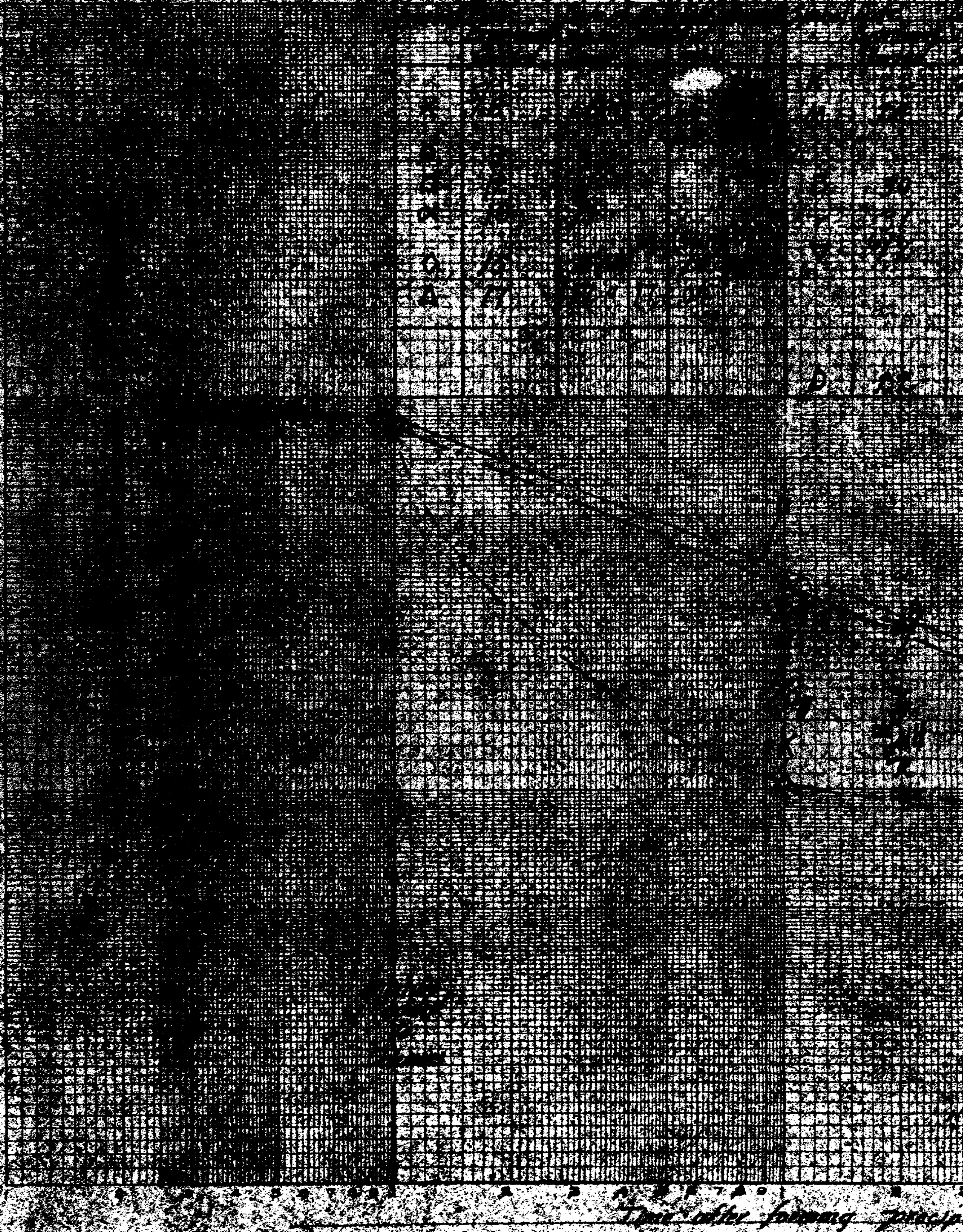


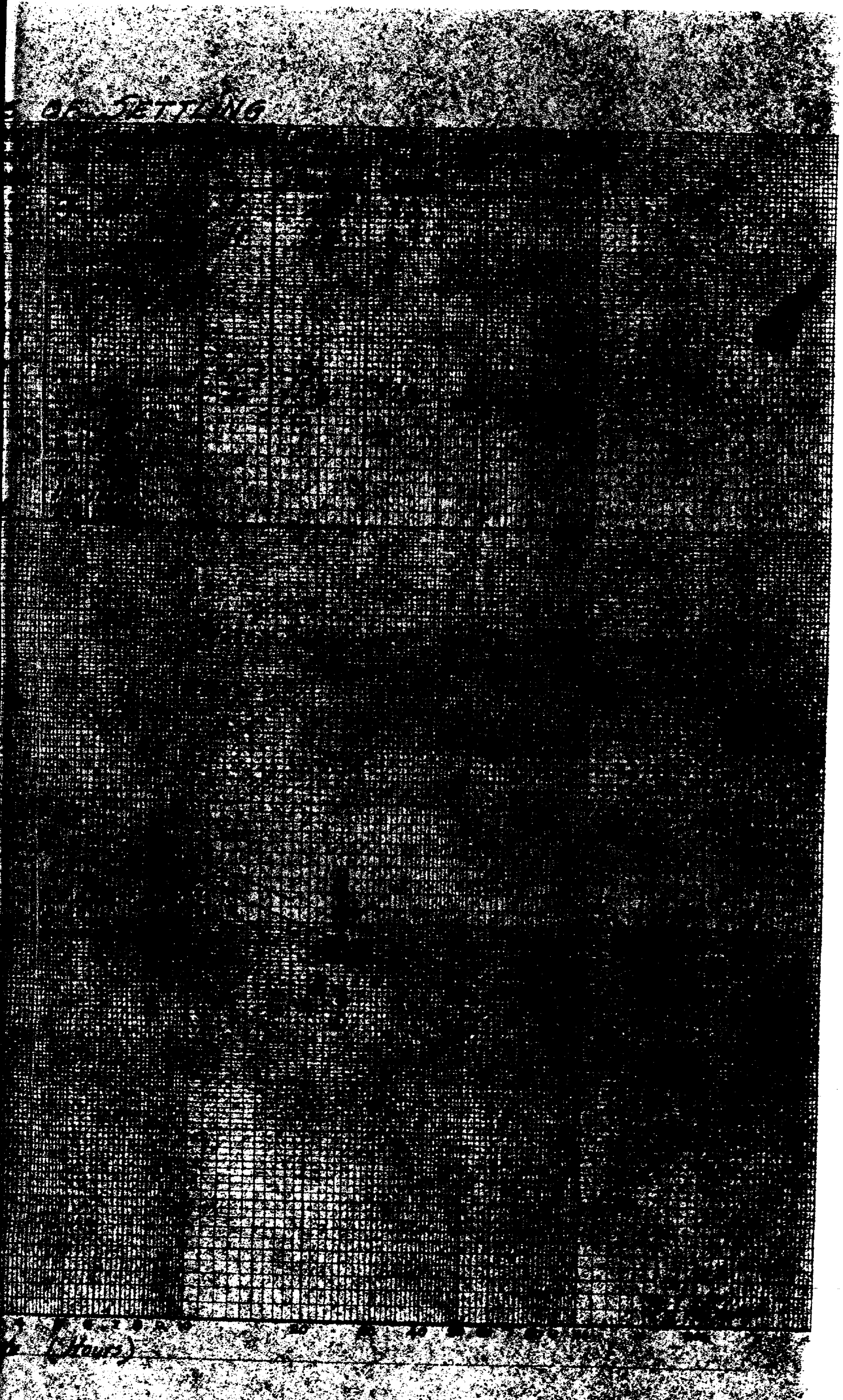
FIGURE 1: ACTIVE WASTE DISPOSAL SYSTEM
By-Product Waste
(4,700 gal./day)
Metal Waste
(1400 gal/day)
W-5
W-7
W-9
W-6
W-8
W-10
180,000 gal. ea. Capacity Tanks (covered)
Solid Lines are for Flowsheet for System Placed in Operation July 2, 1944
Dotted Lines Indicate System March 6 to April 27
(10,000 gal./day)
(4,700 gal/day)
Plant Cooling Water
(900,000 gal./day average) not regulated
West Pond
East Pond
200,000 gal. ea. Capacity Ponds
Diversion Box
Inlet Weir
NEW Basin
1,500,000 gal. Cap. 200'x200'x5'
Floating Frame-Work
Outlet Weir
Clinch River (200 cu. ft. per sec. guaranteed minimum) (about 25,000,000 cu. ft.)
Reservoir
Dam
Estimated Flow from 5-10 ft³/sec
2 miles
White Oak Creek
7/14/44 J.T. Weills

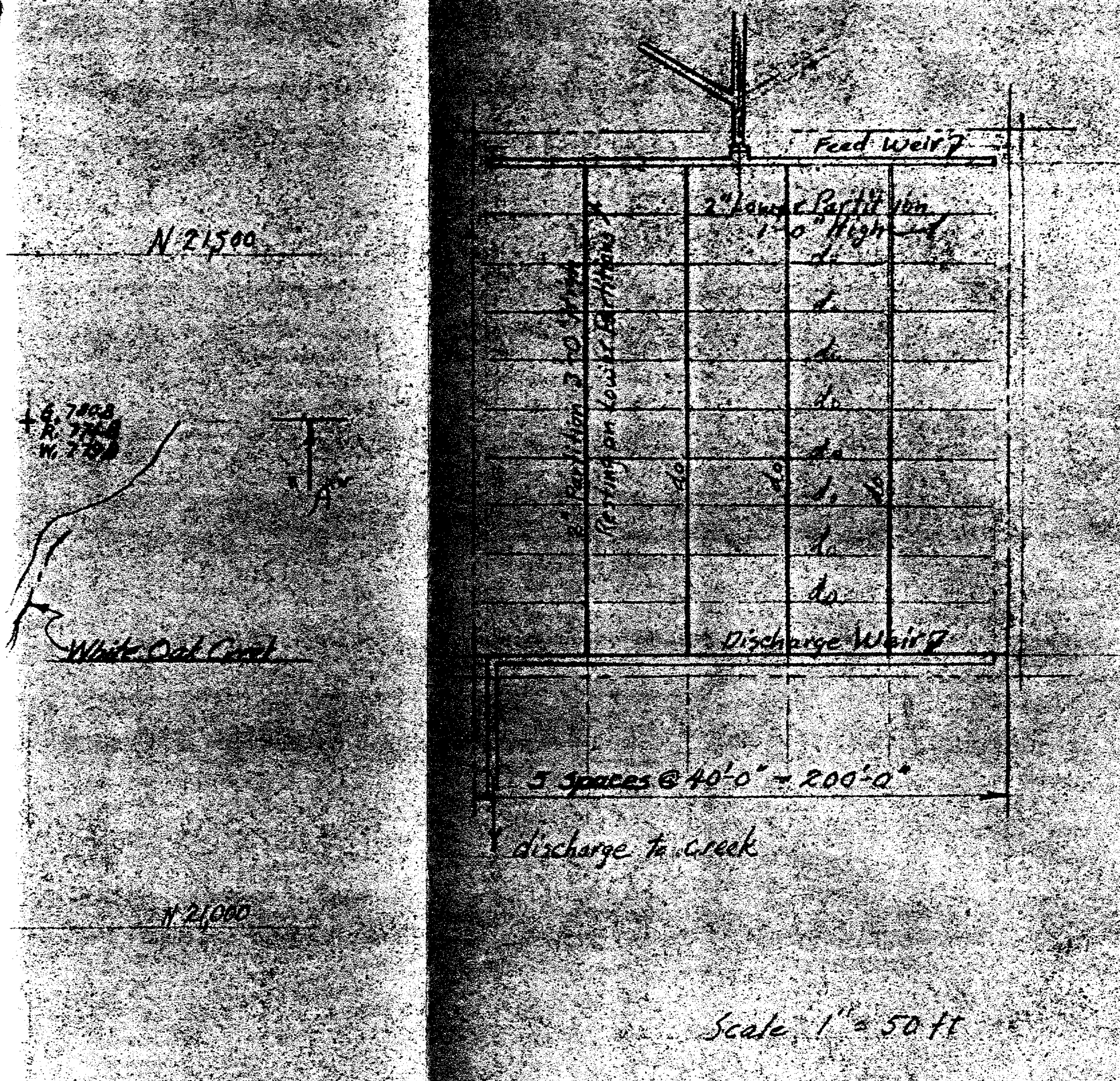


X = Precipitate formed on ...
100
80
60
40
20
10
Compaction (% of Unpacked Height)
10
20
40
50
100
200
400
Precipitate Added (cm. of Unpacked Height)

FIGURE [illegible] DECONTAMINATION VS TIM[illegible]

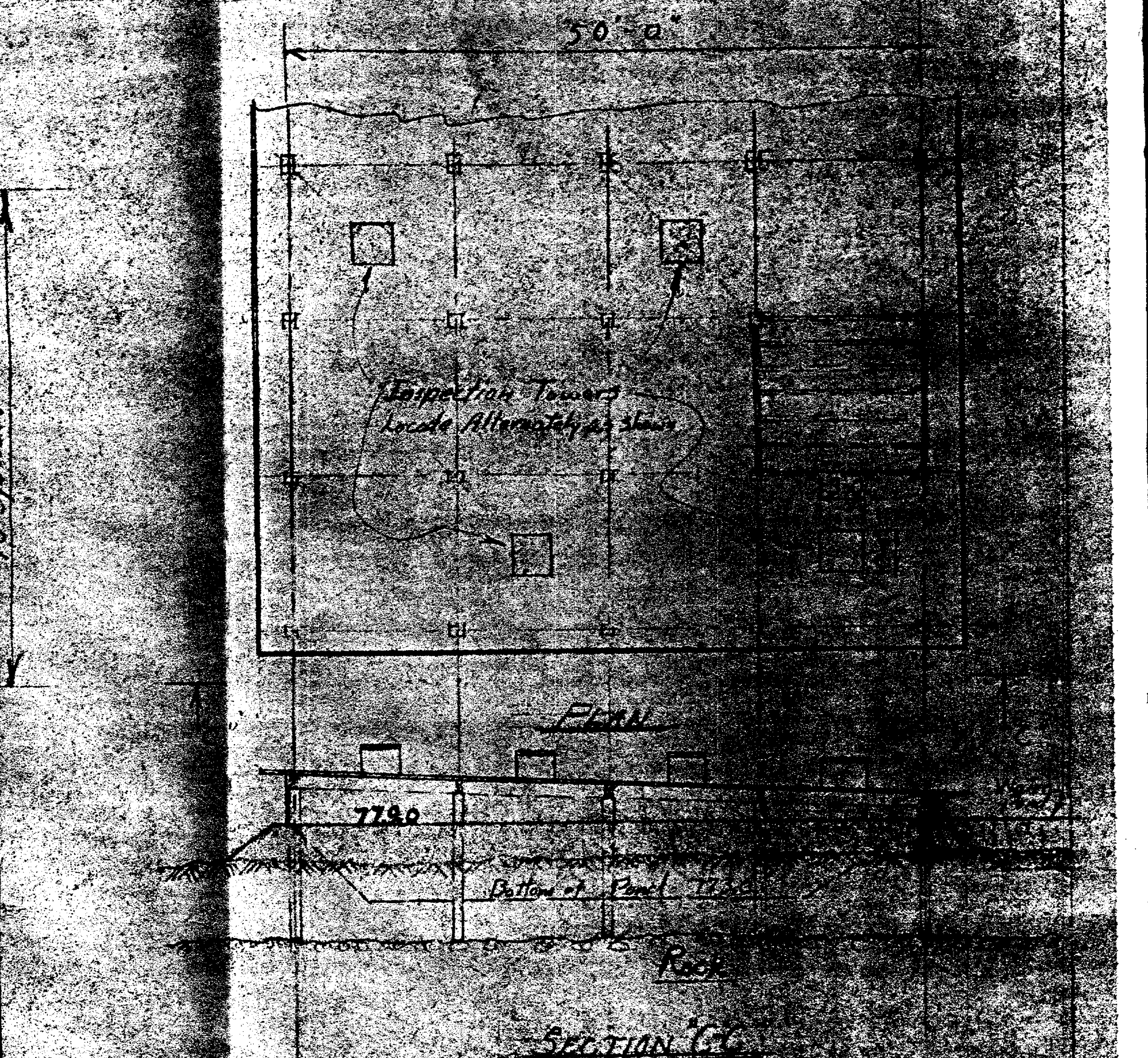



OF SETTLING
(Hours)



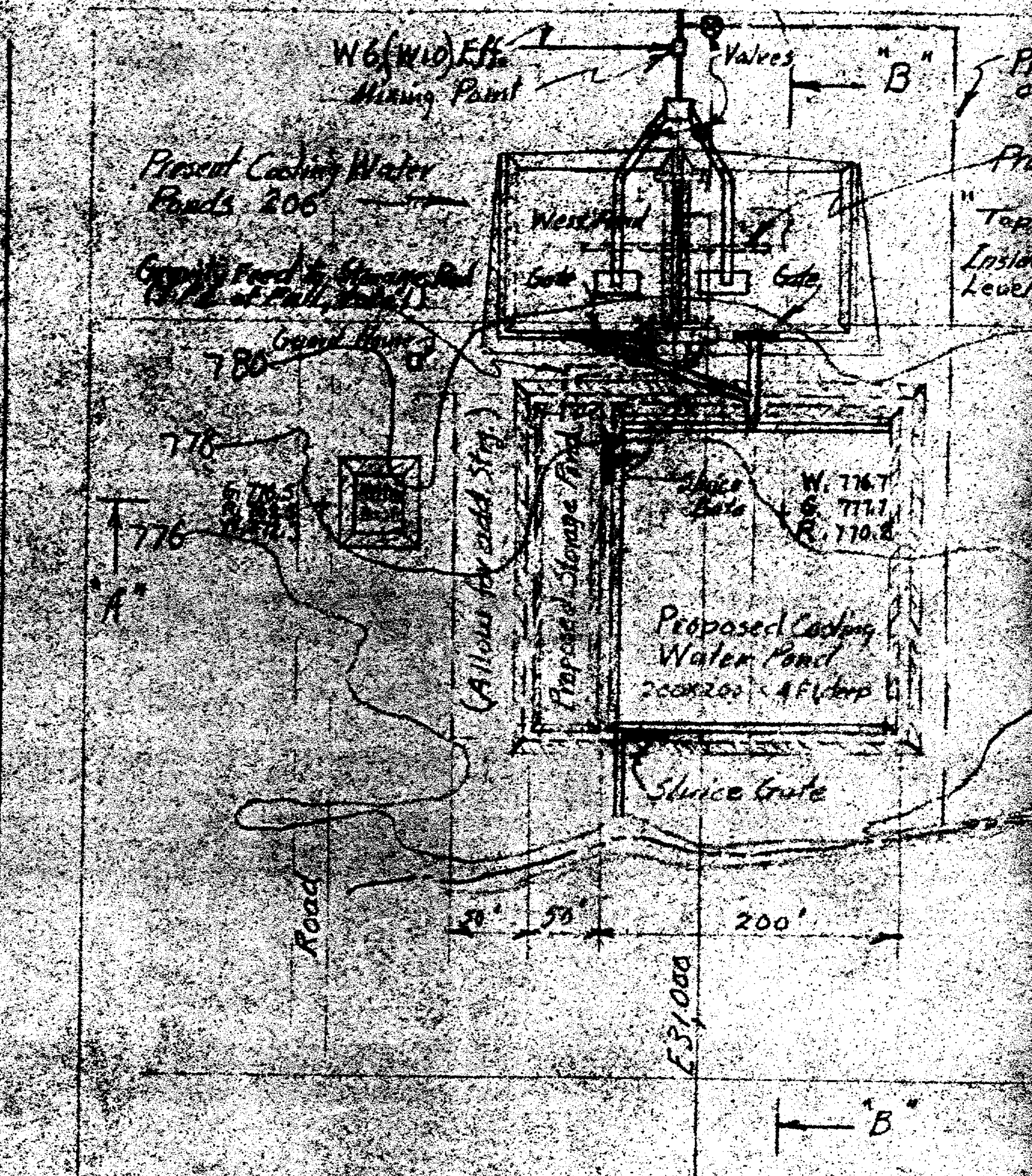
CHANGES

PLAN OF PROPOSED WATER POND



PLAN & EL OF STORAGE POND

Scale 3/32 1



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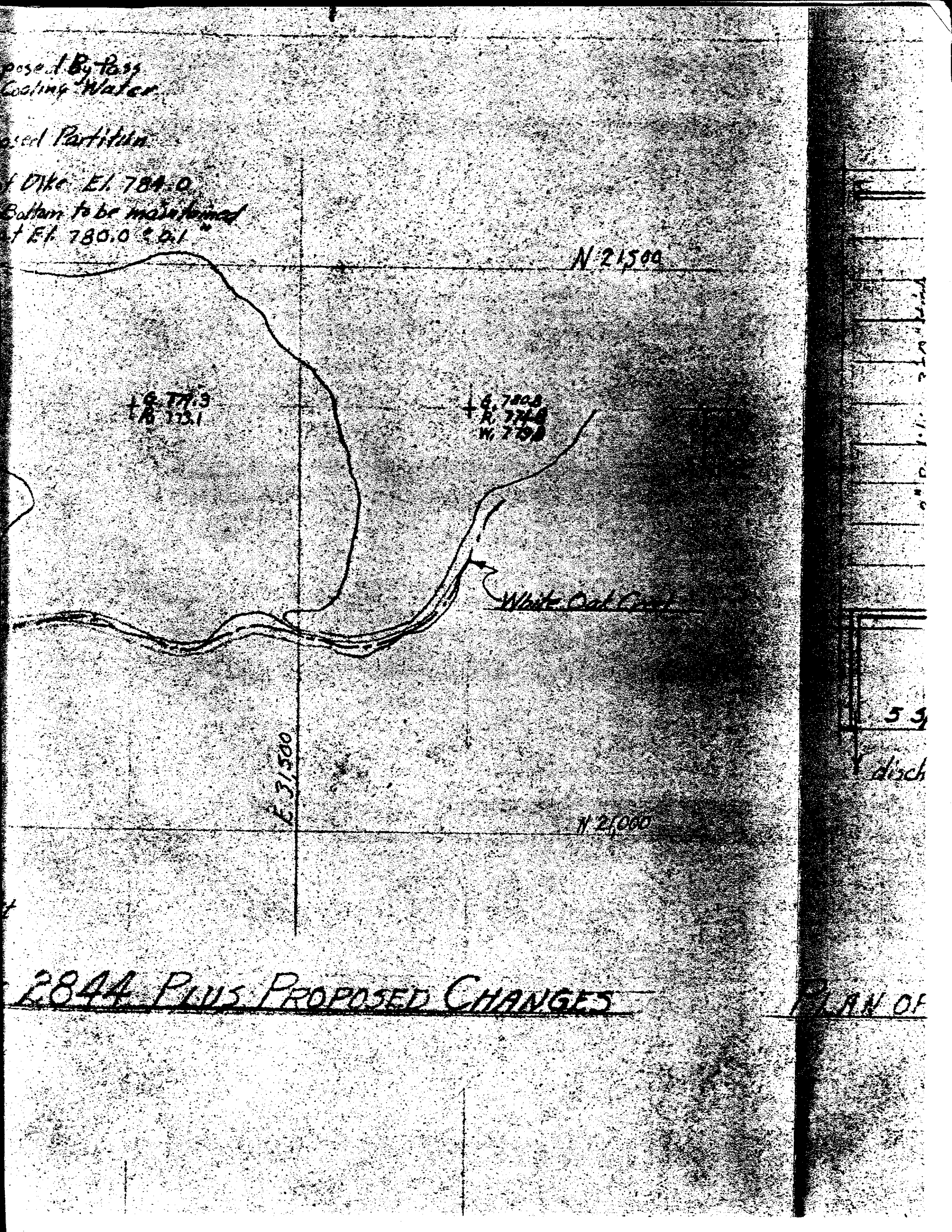
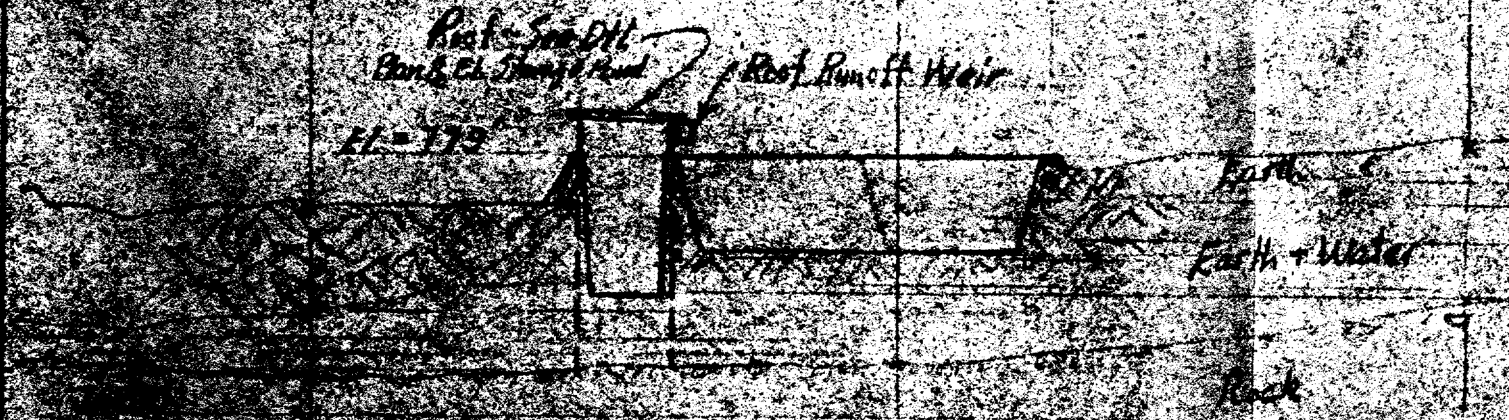
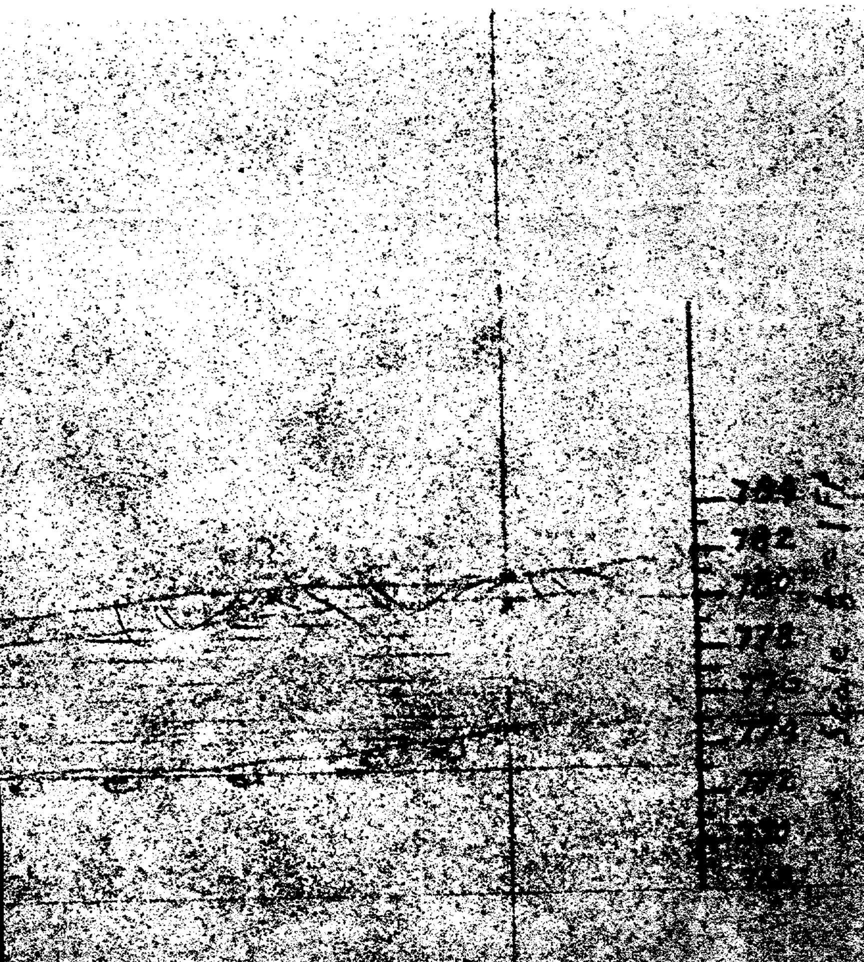

posed By Pass
Cooling Water
osed Partition
f Dike El. 784.0
Bottom to be maintained
t El. 780.0 ± 0.1
N 21,500
White Oak Creek
E 31,500
N 21,000
5 3
disch
2844 PLUS PROPOSED CHANGES
PLAN OF



Scale Horizontally 1" = 100 Ft

SECTION "A-A"

[illegible] elevations in field including creek level, rock, [illegible] and [illegible]
[illegible] gate to drain Proposed Water Pond [illegible] Level [illegible]
[illegible] Storage Pond to Drain [illegible] Level [illegible]
[illegible] Present Ponds to [illegible] Level [illegible]
[illegible] Level [illegible]
[illegible] possibility of adding to Storage Pond
[illegible] of Storage [illegible] Proposed Water [illegible]
[illegible] West because of high [illegible] Table.
[illegible] entire Length of Storage Pond, Provide [illegible]

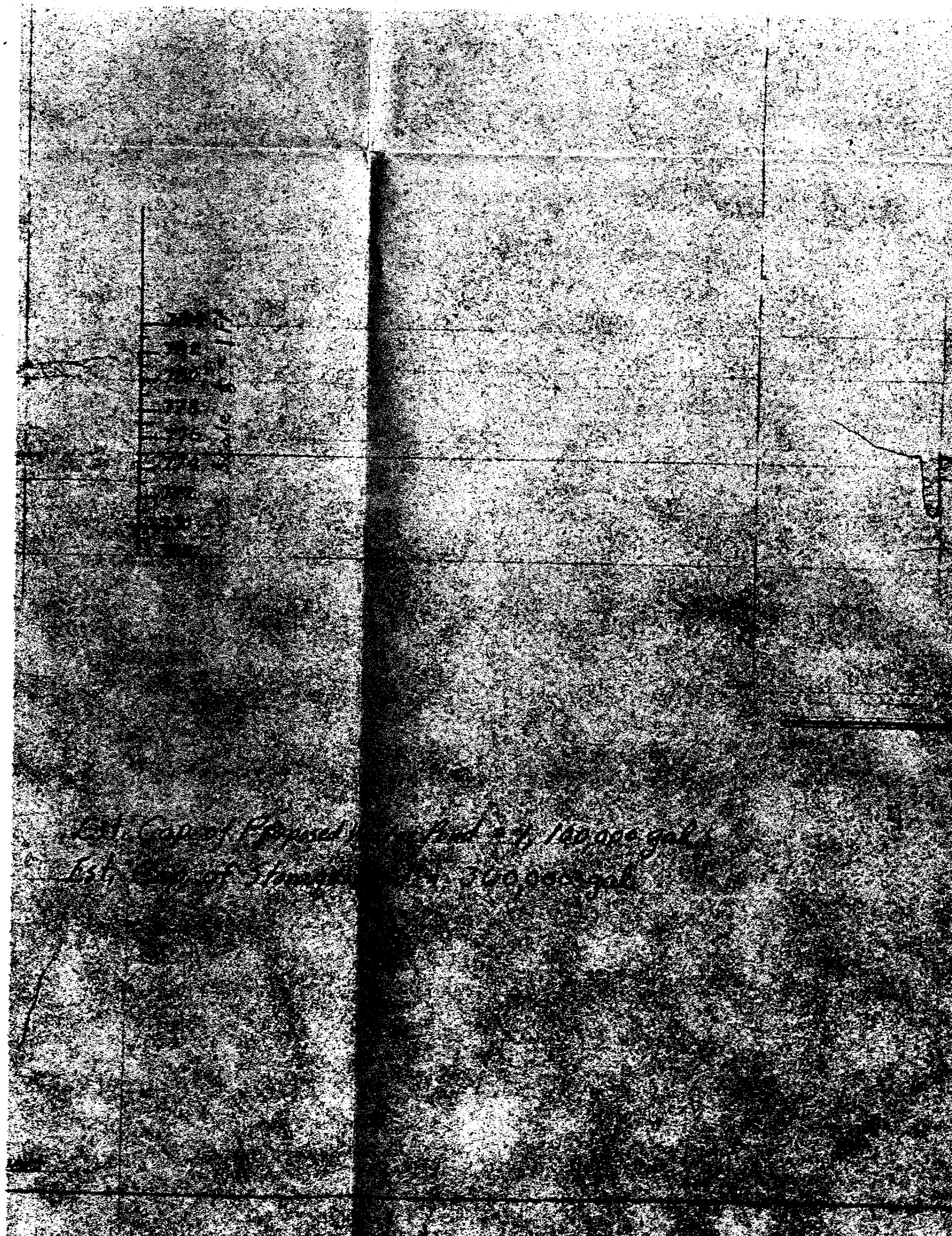


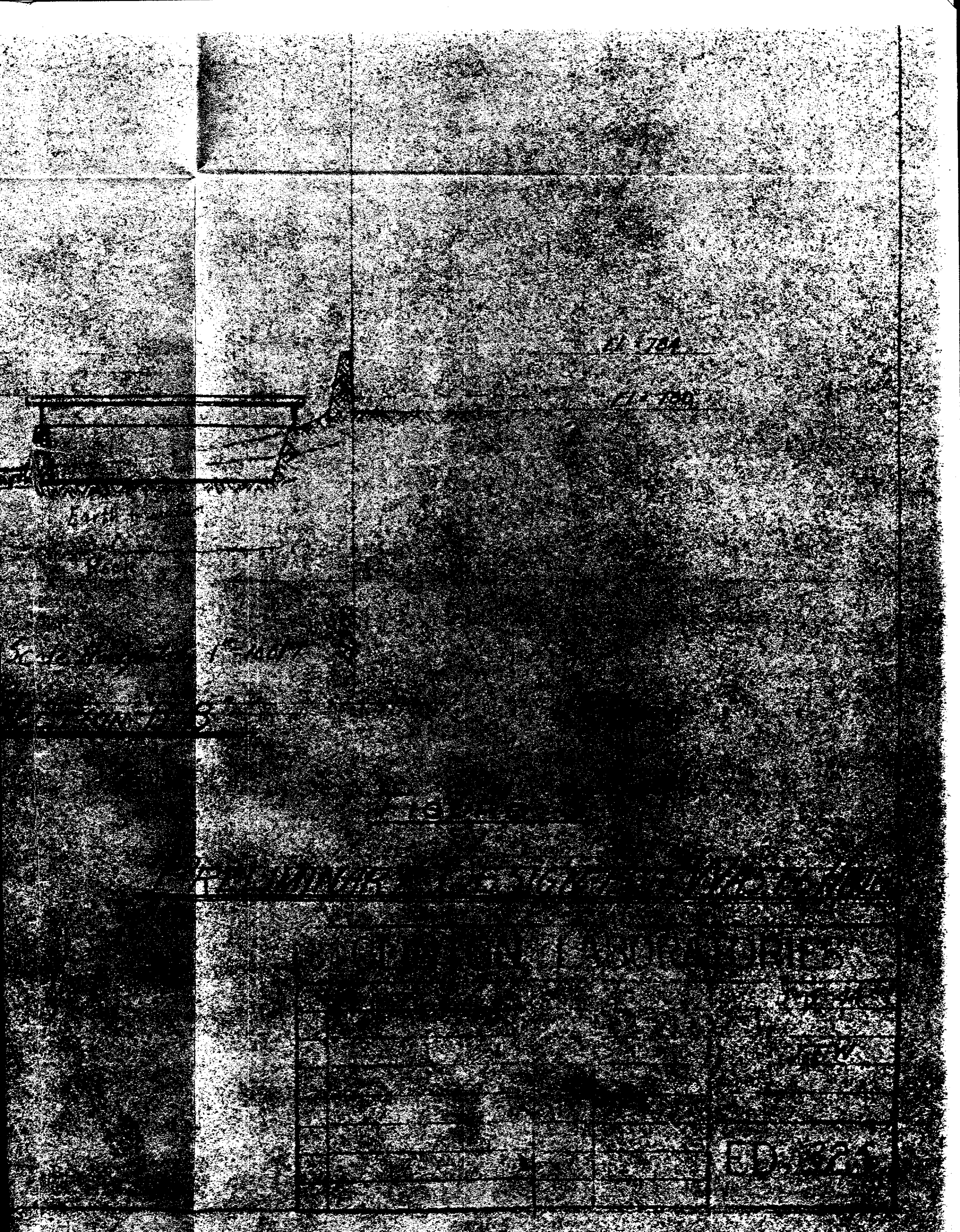
...d Lands

Est. Cap. of Proposed [illegible] 1,100,000 ga

Est. Cap. of Stomge [illegible] gal.

[illegible] Inspection Towers


778
776
774
Est. Cap. of Proposed
Pond = 1,140,000 gal.
Est. Cap. of Storage
300,000 gal.



Earth
Rock